polymer reports

Ruthenium tetroxide as a staining agent for unsaturated and saturated polymers

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INTRODUCTION

Osmium tetroxide is the most important staining agent in transmission electron microscopy (*TEM*) studies of elastomeric blends, unsaturated latices and some high impact resins[1]. By fixing and staining the unsaturated rubber phase at the same time it allows easy ultramicrotomy of the sample and greatly enhances the contrast between the phases in *TEM*.

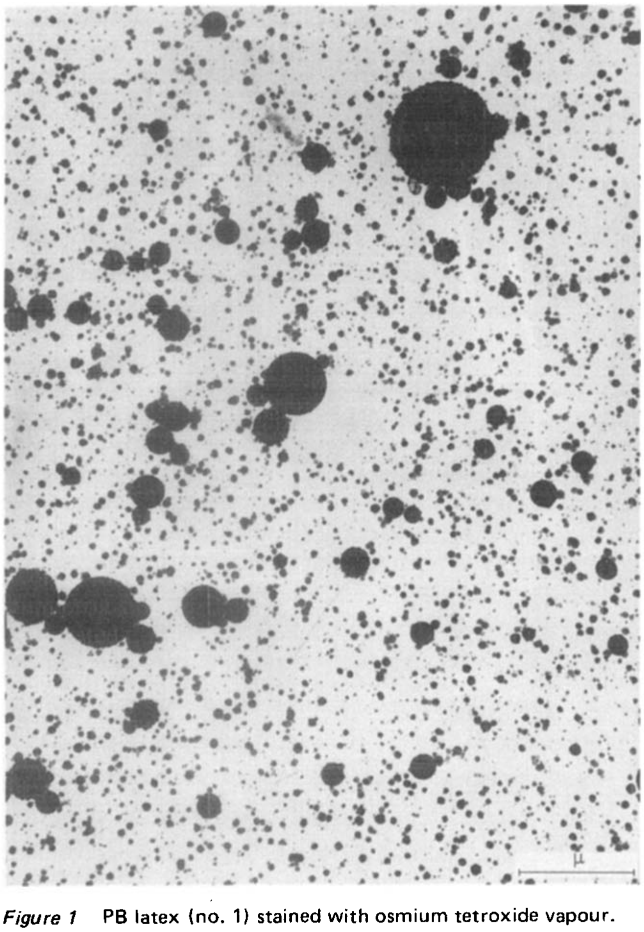

Figure 1 PB latex (no. 1) stained with osmium tetroxide vapour. 30 000X

ABS resins have been shown to be heterogeneous and the particle dimensions in unsaturated latices could also be measured accurately.

Problems result from the low diffusion of OsO_4 in polymers. In the ABS resins, for instance, hardened layers of only a few μm can be obtained, and a thinner layer results with PVC–MBS blends. Saturated polymers as ASA are not stained at all.

In latices thin osmium-induced precipitates can easily be confused with the smallest polymer particles and a less exact determination of the particle size results. In order to avoid these difficulties with OsO_4 we have used RuO_4 as an alternative staining agent. This reagent was chosen because of its high reactivity with some organic substances[2]. A preliminary investigation on PB latices, ABS and ASA resins has been undertaken in our laboratory using a 1% water–RuO_4 solution.

EXPERIMENTAL

Polybutadiene latices

Two samples of *cis*-1,4-polybutadiene latex, diluted in distilled water, were placed on a microscopy grid and treated for 20 min with the vapour from a 1% OsO_4–water solution. *TEM* micrographs of the two samples are shown in *Figures* 1 and 2. The effects of the finely divided precipitates, covering and masking the smallest polymer particles, are evident.

Samples of the same latices were subsequently treated with vapours from a 1% RuO_4–water solution. After 20 min treatment a precipitate even more extensive than that resulted after OsO_4 treatment was observed. Since this might be due to the high reactivity and instability of RuO_4, the staining time was shortened. *TEM* micrographs obtained after a 3 min RuO_4 treatment are reported in *Figures* 3 and 4.

The two staining systems are substantially equivalent as far as particle morphology is concerned. Little difference in the amount and shape of the precipitates (thinner, less-masking particles) seems to favour the RuO_4 treatment.

ABS resin

Two samples of the same ABS (18% rubber content) were stained for 3 days in 1% OsO_4–water solutions,

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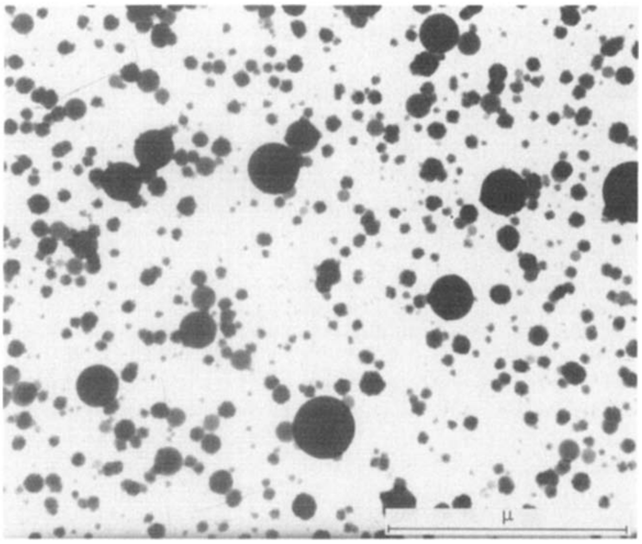

Figure 2 PB latex (no. 2) stained with osmium tetroxide vapour. 60 000X

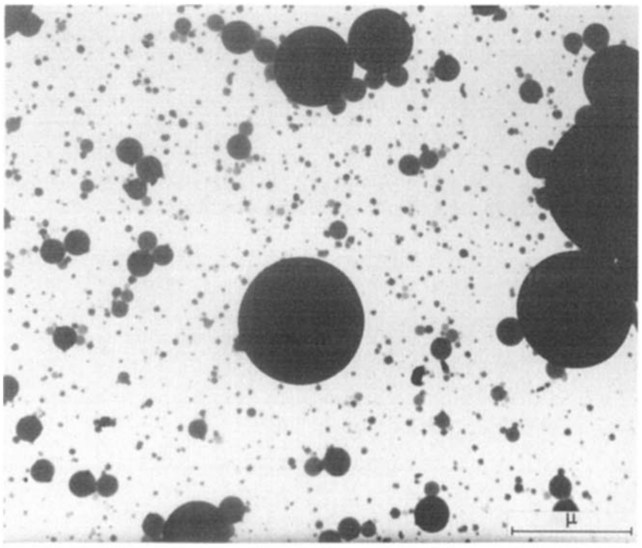

Figure 3 PB latex (no. 1) stained with ruthenium tetroxide vapour for 3 min. 30 000X

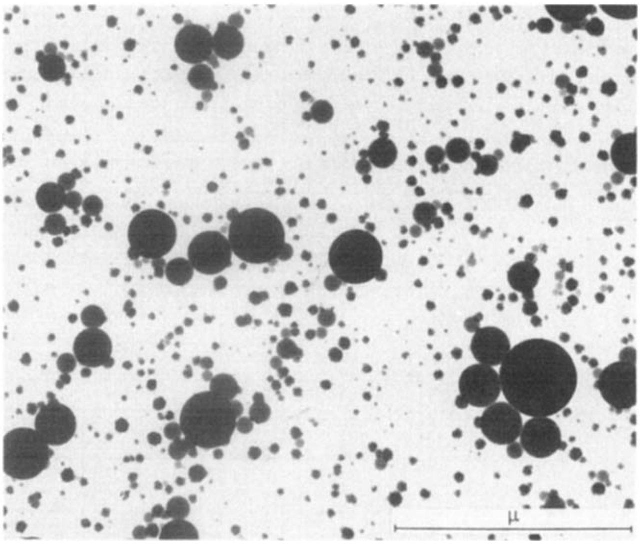

Figure 4 PB latex (no. 2) stained with ruthenium tetroxide vapour for 3 min. 60 000X

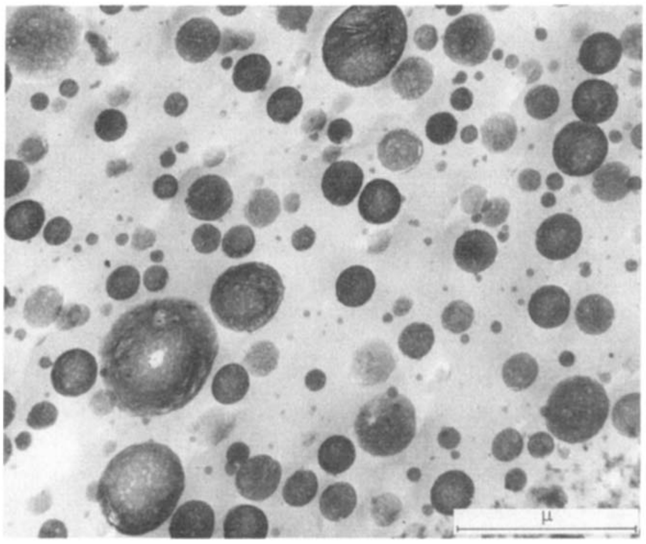

Figure 5 Thin section of ABS resin stained with ruthenium tetroxide. 45 000X

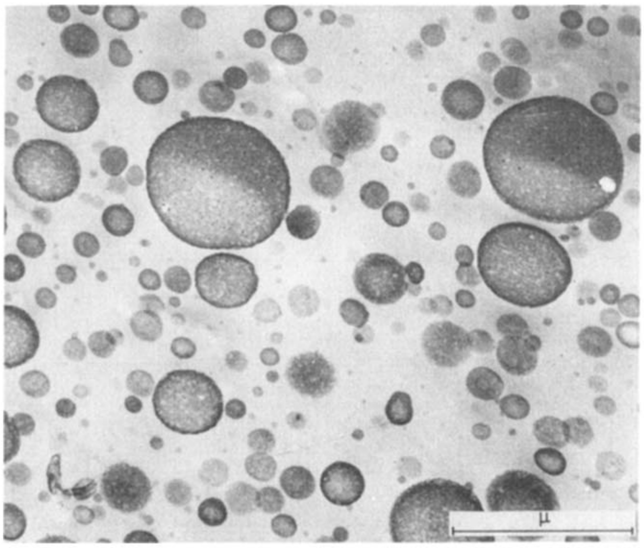

Figure 6 Thin section of ABS resin stained with osmium tetroxide. 45 000X

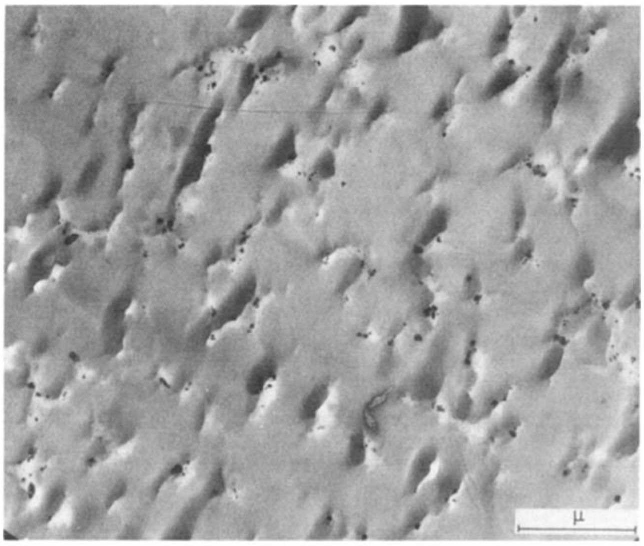

Figure 7 Thin section of ASA resin stained with osmium tetroxide. 30 000X

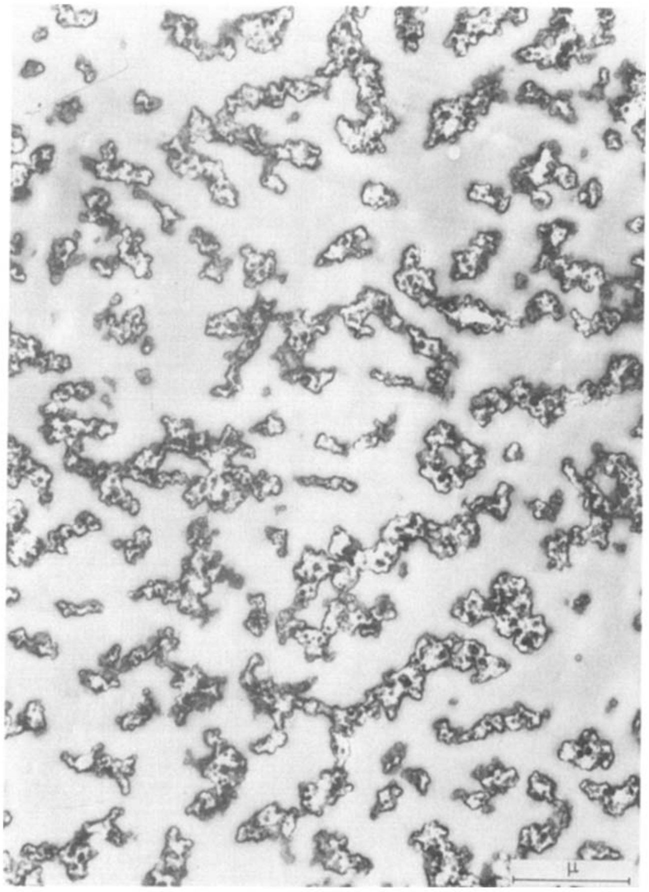

Figure 8 Thin section of ASA resin stained with ruthenium tetroxide. 30 000X

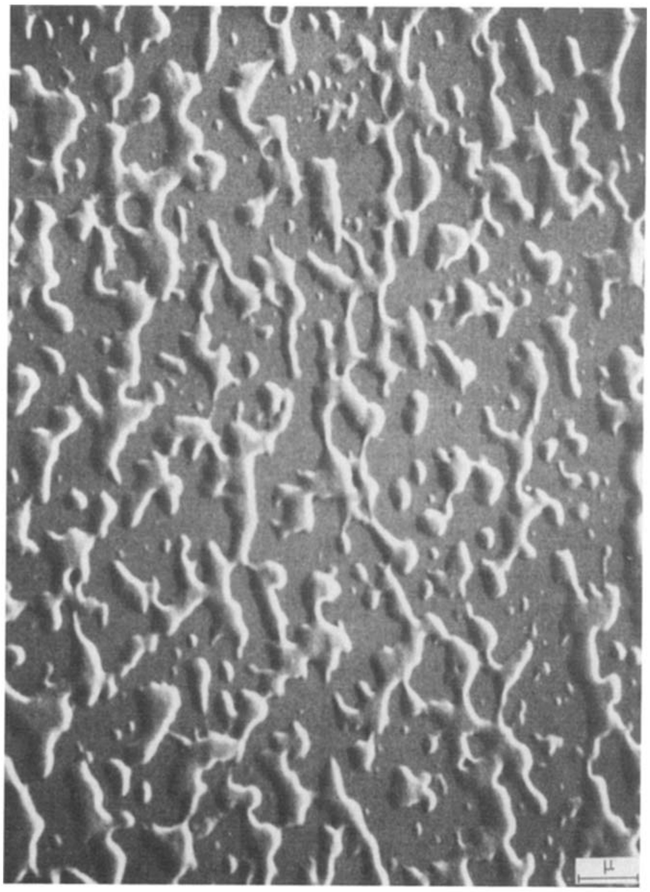

Figure 9 *SEM* micrograph of ASA resin section etched with alcohol–acetone mixture. 15 000X

respectively. The samples were ultramicrotomed and examined by *TEM* (*Figures* 5 and 6). The identical morphologies of the rubber phases in these Figures prove that the two stainings are equivalent.

ASA resin

Two samples of the same resin were stained with OsO_4 and RuO_4. Because of the fully saturated nature of the samples no staining action was observed with OsO_4: the sections show irregular surfaces (*Figure* 7) due to modifications of the rubber phase occurring during the ultramicrotomy.

Treatment with RuO_4, however, was unexpectedly successful in hardening and staining the saturated rubber phase. The ease of cutting of the sample and the good characterization of the phases were made possible (see *Figure* 8) through a crosslinking mechanism, probably acting on the ester groups of the acrylate phase. The staining of the rubber phase is evident in this *Figure*. The effect is greater at the boundary than at the centre of the dispersed particles probably because of a low diffusion rate for RuO_4 into the rubber.

Thin sections of the same material have also been observed by scanning electron microscope, after chemical etching with alcohol–acetone mixtures[3].

The substantial morphological similarity seen in the micrographs (*Figures* 8 and 9) seems to be proof of the reliability of treatment with RuO_4.

CONCLUSIONS

Ruthenium tetroxide behaves as a hardening and staining agent for saturated rubbers where Osmium tetroxide is ineffective. A preliminary investigation has been reported, in which the morphology of an ASA resin was clearly determined after treatment with an RuO_4–1% water solution. The mechanism by which RuO_4 acts to harden and stain saturated rubbers has not yet been explained, but reaction with the ester groups of poly(butyl acrylate) seems likely to be involved. RuO_4 hardens and stains the unsaturated rubber in the same manner as OsO_4.

The experimental data presented in this work, indicate that RuO_4 is a more general staining agent than OsO_4 for *TEM* investigations.

REFERENCES

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